Electrochemical performances of vitreous materials in the system Li_2O–V_2O_5–P_2O_5 as electrode for lithium batteries

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ABSTRACT

Glass composition $25Li_2O$ $50V_2O_5$ $25P_2O_5$ has been investigated as a potential material for electrode. Electrical properties as well as electrochemical performances of this glass composition have been characterized and results show a capacity less than 80 mAh g^{-1} when tested in the [3 4.5 V] potential window. To the best of our knowl edge, this is the first lithiated amorphous material reported as a potential positive electrode material. Glasses, due to their wide available compositions in a given system and their easy processing, pave the way to new type of electrode material.

1. Introduction

The materials investigated to find new suitable intercalation host structures for applications in Li or Li ion batteries are essentially crys talline materials. Glass compositions have also been investigated as potential electrode material but mainly as solid electrolyte essentially for all solid state batteries in the 80's [1 4] and, as shown by papers in the last 10 years, these glassy materials are still under interest [5 9]. Only few glass systems have been investigated for their poten tiality as positive electrode material among which we can cite the V_2O_5 P_2O_5 system which exhibits high capacity and a good reversibility [10] or the TeO_2 V_2O_5 system [1]. To the best of our knowledge most of ternary glasses including lithium have been studied essentially for their electronic/ionic conductivity like in many oxide glasses such as Li_2O B_2O_3 V_2O_5 [11], Li_2O MoO_3 P_2O_5 [12], Li_2O V_2O_5 TeO_2 [13] or in chalcogenide glasses [14]. These studies have been more recently extended to the glass ceramics and on the effect of nano crystallization on the conductivity [15,16]. However, they have never been tested as electrode material.

In our study, the Li_2O P_2O_5 V_2O_5 ternary system has been selected as possible electrode materials for rechargeable lithium batteries. This ternary system exhibits a large vitreous domain leading to a wide choice of glass compositions [15] allowing, once understood, the relationship structure properties to adjust their composition to optimize the desired properties. Despite taking place in air, during the synthesis, a spontane ous reduction of V^{5+} down to V^{4+} is observed leading to samples including both Li^+ and V^{4+} ions. Therefore, some electrochemical activ ity in charge can be expected. Moreover these samples exhibit mixed ionic/electronic conductivity [17] the former occurring via transport of Li^+ while the latter consists in the electron hopping between V^{4+} and V^{5+} centers. Some studies [18] have revealed that the conductivity switches from mainly electronic for high vanadium content samples to mainly ionic for high lithium content samples. Intermediate compo sitions correspond to mixed electronic/ionic conductivity. Then, to combine both possibilities of lithium extraction via V^{4+} oxidation and the advantage of mixed conductivity, the special composition $25Li_2O$ $50V_2O_5$ $25P_2O_5$ has been selected to investigate the electro chemical properties of such this glass. Samples are prepared and their thermal behavior as well as electrical properties has been determined. Electrochemical behavior both in oxidation and reduction modes are in vestigated while soft chemistry routes are used to mimic fully oxidized and reduced samples. The interpretation of all the different results con firms the potentiality of such ternary glasses as possible candidate for electrode materials in Li ion batteries.

2. Experimental

2.1. Glass synthesis

Glass composition $25Li_2O$ $50V_2O_5$ $25P_2O_5$ (molar fraction) is pre pared by mixing in a mortar a batch of 2 g of appropriate amount of commercially Li_2CO_3 (Alfa Aesar, 98%), $(NH_4)_2HPO_4$ (Merck, 98%) and V_2O_5 (Aldrich, 99.6%). The precursors are heated at 400 °C in a platinum crucible to decompose the carbonate and the di ammonium hydrogen phosphate. The product is then mixed again for a better homogenization

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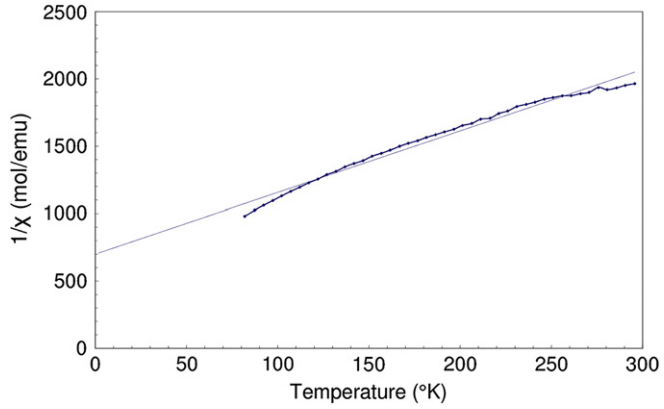

Fig. 1. The thermal variation of the inverse magnetic susceptibility in the $25Li_2O$-$50V_2O_5$-$25P_2O_5$ glass composition measured with a field of 7600 G. The dashed line represents the Curie-Weiss law.

and the temperature is increased to 900 °C for melting. The melt is kept for 1 h at this temperature and then quenched between two stainless steel plates to obtain glassy sample. For conductivity measurements, samples are molded in a circular shape and annealed 1 h at Tg 10 °C to remove the mechanical stress occurring during quenching. The tem perature is then decreased slowly to room temperature. The chemical composition of the glass after synthesis is checked by microprobe SX 100 CAMECA. Thin platinum layer are then pasted on each face of pellets to ensure good electrical contact.

2.2. Physical measurements

Thermal characteristics of the glass (glass transition temperature, Tg and crystallization temperature, Tc) are determined using a DSC Mettler equipment (heating rate: 10 °C/min).

XRD patterns have been recorded using a D8 Bruker equipment in the range 10 55° (2θ). Ex situ measurements on charged/discharged materials have been performed using a cell with Be window.

Impedance measurements are performed in the range of tempera ture 300 K 470 K under helium using a HP4192A Impedance Analyzer working in the frequency range 5 5×10^6 Hz. Prior to the measure ments, a Pt layer is deposited on each side of the glass bulk.

The influence of ball milling on the glass particle size have been observed using Scanning Electron Microscopy (FEG SEM JEOL 7400 F).

The presence of mixed valence is determined according to the magnetic susceptibility experiment based on the Faraday's method in the range of temperature 73 K 300 K.

2.3. Electrochemical tests

For electrochemical tests, the $25Li_2O$ $50V_2O_5$ $25P_2O_5$ glass is ground with 15%wt of SP carbon (Black carbon from MM, Belgium) in a planetary ball mill (Fritsch) for 2 h using tungsten carbide (WC) bowl and balls. The mixture (7 10 mg) is used as positive electrode and placed in a Swagelok™ cell using a Whatman GF/D borosilicate glass fiber sheet saturated with a 1 M $LiPF_6$ electrolyte solution in 1:1 dimethyl carbonate (DMC)/ethylene carbonate (EC) and a Li foil as negative electrode. Elec trochemical characterizations are carried out in galvanostatic mode using VMP 2 multichannel potentiostat/galvanostat (Biologic Co, Claix, France). A cycling rate of C/10 (1 lithium in 10 h) is used. In potential composition curves, x corresponds to the number of moles of Li involved in the discharge/charge of the electrode.

Chemical extraction or lithiation of $25Li_2O$ $50V_2O_5$ $25P_2O_5$ glass are performed to mimic the electrochemical oxidation or reduction process. One mole lithium is extracted from the pristine glass by using 1 M NO_2BF_4 acetonitrile solution as the oxidizing agent; the NO_2^+/NO_2 couple being the active redox couple, while the BF_4^- ions solely act as spectators. Up to six moles of lithium are inserted in the pristine glass by using butyllitium (C_4H_9Li) in cyclohexane as the reducing agent. The experiments are conducted at 80 °C in an argon dry box by placing in a glass vessel 0.5 g of glass and pouring the exact amount of oxidizing or reducing agent. The solutions are stirred for 48 h.

3. Results and discussion

3.1. Magnetic measurements

The magnetic susceptibility χ (T) is measured in a field of 7600 G in the temperature range 80 300 K. The thermal variation of 1/χ (Fig. 1) follows a Curie Weiss law with a paramagnetic Curie temper ature $\theta p \approx -153$ K. The magnetic measurements (Faraday balance) show a mixed valence V^{4+}/V^{5+} for the $25Li_2O$ $50V_2O_5$ $25P_2O_5$ glass composition. The total Curie constant, C_t, is calculated from the relation ship $\chi \quad \frac{C_t}{T}$ with T, the temperature in °K. At 295 K under 7600 G, the total Curie constant, C_t is equal to 0.151. The Curie constant of V^{4+} is 0.375 which leads to an amount (atomic %) of V^{4+} of about 40% in the $25Li_2O$ $50V_2O_5$ $25P_2O_5$ composition. Thus, this composition can be written as following $Li_2(V^{4+}{}_{0.4}V^{5+}{}_{0.6})_4P_2O_{15.2}$ and more generally as

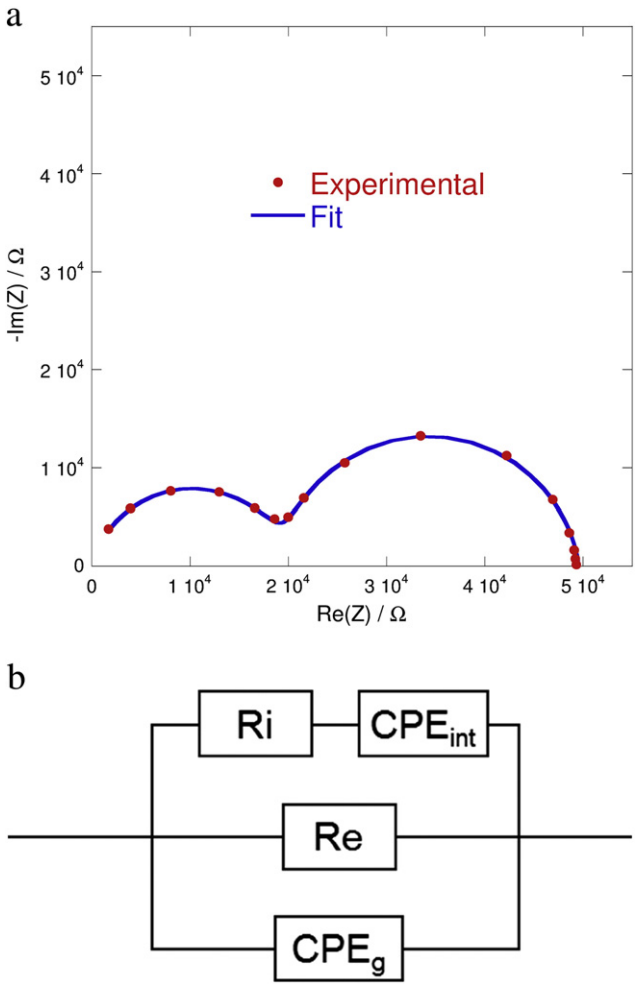

Fig. 2. (a) Impedance measurements of glass bulk composition $25Li_2O$-$50V_2O_5$-$25P_2O_5$: experimental data and fit taking into consideration the Weppner model [20], (b) Maxwell's equivalent circuit.

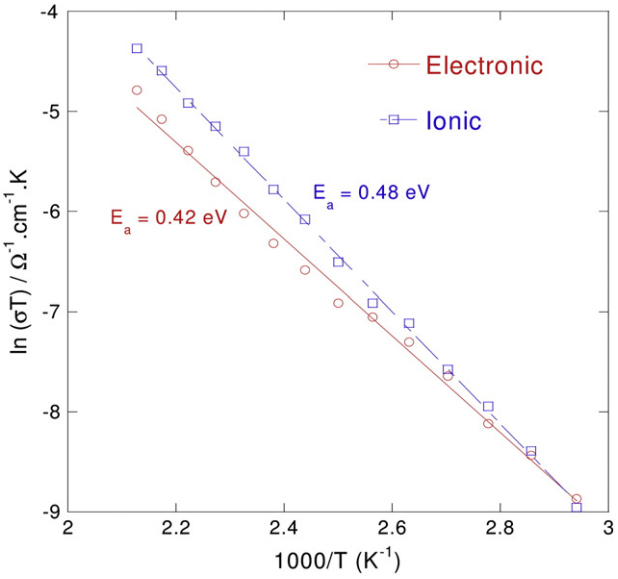

Fig. 3. Arrhenius plots of electrical (ionic and electronic) conductivity of glass bulk composition $25Li_2O\text{-}50V_2O_5\text{-}25P_2O_5$.

$Li_2(V^{4+}{}_yV^{5+}{}_{1-y})_4P_2O_{16-2y}$ to take into account the charge compensation due to vanadium spontaneous reduction. Microprobe analysis confirms the homogeneity of the glass and the ratio V/P. To be more precise, our glass therefore belongs to the quaternary system Li_2O V_2O_5 V_2O_4 P_2O_5.

3.2. Electrical measurements

An example of the results of the AC measurements is shown in Fig. 2a. The Nyquist plots may be decomposed into two semicircles in the mid and high frequencies domain, while there is only a single point on the real axis at the low frequency end. Such diagram is characteristic of a mixed ionic/electronic conductor and it may be represented by the Maxwell's equivalent circuit as reported in Fig. 2b [19 21]. In this circuit, R_e corresponds to the electronic resistance, R_i is the ionic resistance, C_g is the geometrical capacitance, and C_{int} is the interfacial capacitance associated to the ionically blocking Pt electrodes (which is shunted by the electronic current at low frequencies). The non linear least squares fitting program Equivcrt [22] was used to fit the experimental data with this equivalent circuit. The comparison between experimental and fitting data using the Weppner model is reported in Fig. 2a. The R_e and R_i values obtained at each temperature were used to calculate the electronic and ionic conductivity and the corresponding Arrhenius plots are shown in Fig. 3. The results confirm that the base glass composition $25Li_2O$ $50V_2O_5$ $25P_2O_5$ is a mixed electronic/ionic conductor with activation energy of 0.42 eV and 0.48 eV for the electronic and ionic contributions respectively. These values are in good agreement with previously published data on the same composition [18]. However, the extrapolation at room tempera ture indicates the ionic and electronic conductivities are relatively low about 5×10^{-8} $S.cm^{-1}$, which will be a drawback for the electrochem ical performances of this glass. It then appears necessary to optimize the electronic conductivity of the electrode by a homogeneous mixing with carbon black, while small particles size would allow circumventing the low ionic conductivity.

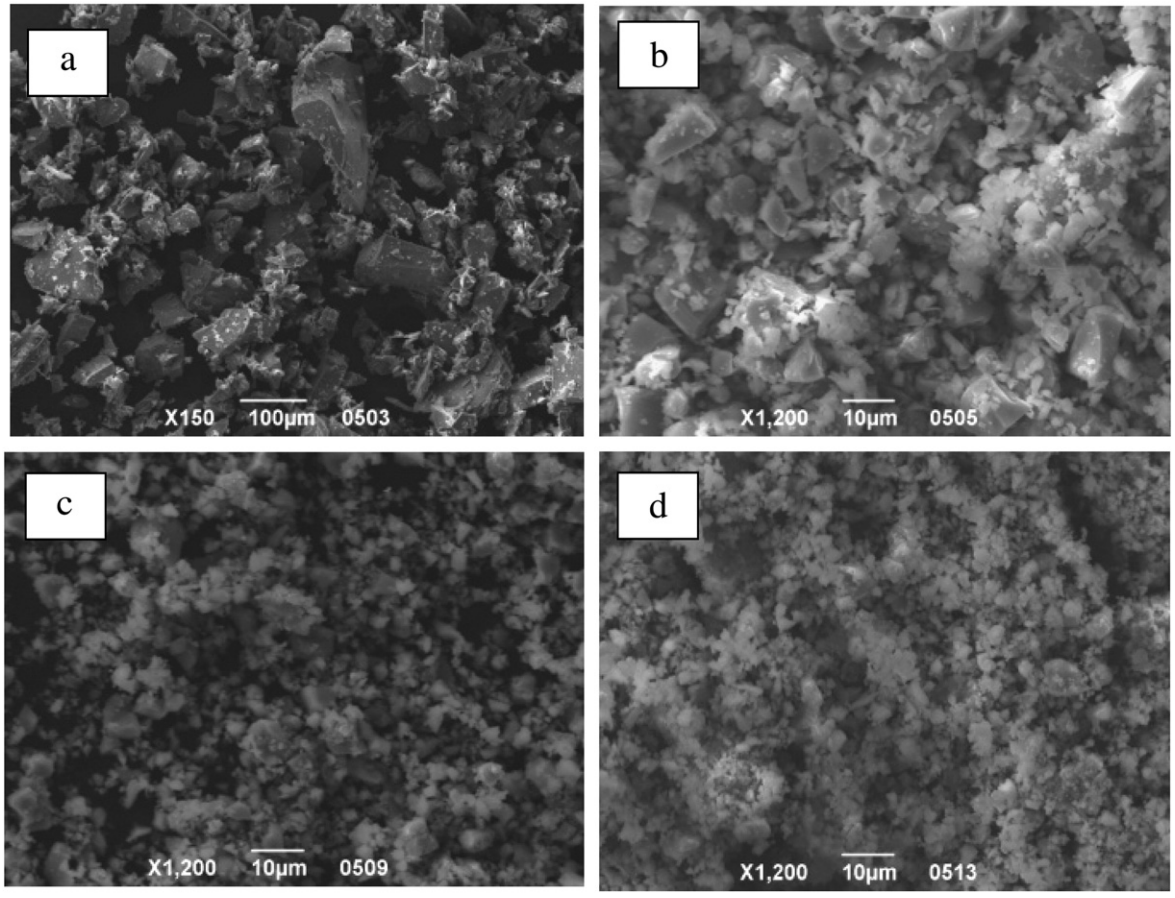

Fig. 4. SEM pictures of the $25Li_2O\text{-}50V_2O_5\text{-}25P_2O_5$ glass composition (a) after hand grinding (b) 30 min planetary ball milling (tungsten carbide jars) (c) 1 h planetary ball milling (tungsten carbide jars) (d) 2 h planetary ball milling (tungsten carbide jars).

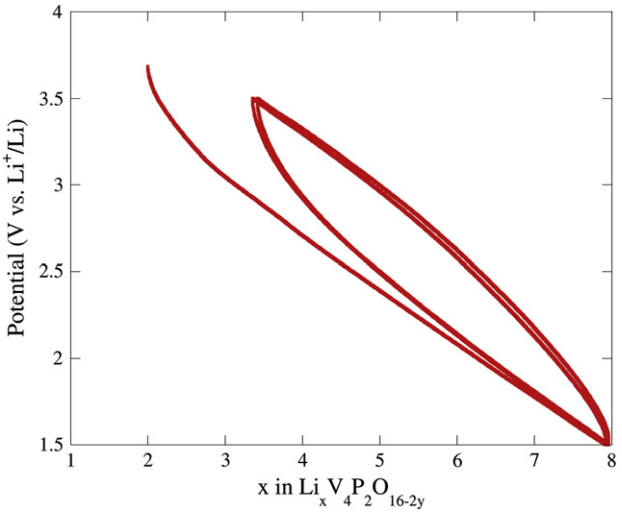

Fig. 5. Galvanostatic charge/discharge curves of the $25Li_2O$-$50V_2O_5$-$25P_2O_5$ glass composition + 15%wt C for a voltage window [1.5-3.5 V].

3.3. Electrochemical performances of the $25Li_2O$ $50V_2O_5$ $25P_2O_5$ glass ($Li_2V_4P_2O_{15.2}$)

Glass pieces are first hand ground in an agate mortar to obtain glass powder (Fig. 4a). Then ball milling is performed on this powder under argon using tungsten carbide (WC) bowl and balls. The SEM pictures revealed after 30 min very big particle size (>10 μm) as well as an inhomogeneous particle size distribution (Fig. 4b). After 1 or 2 h ball milling, the particle size distribution becomes homogeneous and the mean particle size is less than 3 μm (Figs. 4c, 4d). The glass is then mixed with 15%wt. of Carbon SP (Timcal) in a ball milling equipment and tested electrochemically in Swagelok™ type cells against Li metal with 1 M $LiPF_6$ electrolyte solution in 1:1 (w/w) of dimethyl carbonate/ethylene carbonate. A VMP2 automatic cycling/data recording system (Biologic SA, Claix, France) operating in galvanostatic mode at C/10 regime, is used for the electrochemical experiments. The glass is tested at low potential in the voltage window [1.5 3.5 V] and at high potential in the voltage window [3 4.5 V].

Fig. 5 shows the galvanostatic charge discharge curves of the first three cycles of the glassy electrode with the cut off voltage 1.5 3.5 V. The capacity reaches 320 $mAh.g^{-1}$ upon the first discharge with an uptake of six lithium per formula unit, leading to a material with almost all the vanadium in the +3 oxidation state. These results are in good agreement with the ones previously obtained on amorphous V_2O_5 P_2O_5 electrode discharged down to 1.5 V vs Li^+/Li [23]. The first charge up to 3.5 V is associated to the extraction of only 4.6 Li per formula unit, which are then reversibly exchanged during the cycles leading to a capacity of 245 $mAh.g^{-1}$. The specific shape of the voltage composition curve indicates, as usually observed for amorphous samples (structural randomness), that no drastic structural changes occur even for large intercalation ratios [24].

Fig. 6a shows the galvanostatic charge discharge curves of the glassy electrode with the cut off voltage 3.0 4.5 V.

Upon the first oxidation up to 4.5 V, about 1 lithium ion is removed from the glass while an uptake of 1.5 lithium ions is observed in the following discharge down to 3 V against Li metal. The lithium removal/uptake is maintained constant upon the following cycles with an associated discharge capacity of about 72 $mAh.g^{-1}$ at an average potential of 3.7 V (Fig. 6b).

To mimic the glass behavior in the charged as well as in the discharged state, chemical extraction or lithiation has been performed on the glass powder. As mentioned in the literature [15], the composition $25Li_2O$ $50V_2O_5$ $25P_2O_5$ is amorphous. To confirm the total amorphous state of the extracted powder which is of interest in this study, ex situ XRD measurements were performed on the initial glass powder and after a charge at 5 V. The results are shown in Fig. 7b. No difference in diffraction patterns is observed between the two powders, which confirm the material remains glassy in the charged state. It is noteworthy that the observed peaks correspond to the Al coated Be window from the ex situ XRD cell (black arrows).

Glass transition temperature Tg and crystallization temperature Tc of the base glass and the chemically extracted/lithiated powder have been determined by DSC measurements (Fig. 7a). The $25Li_2O$ $50V_2O_5$ $25P_2O_5$ composition has a glass transition temperature of Tg = 285 °C and a crystallization temperature of Tc = 385 °C. The chemically extracted and lithiated powders also shows a glass transition temperature indicating the presence of a glassy phase. The difference ΔT = Tc Tg equal or more than 100 °C is a good criterion to define the glass stability (Hruby's criterion). During lithiation and delithiation, we respectively observe a ΔT of 75 °C and 169 °C, ΔT being equal to 100 °C for the pristine glass. Therefore the lithiation phenomenon destabilizes the glass whereas the delithiation seems to stabilize the glass toward the crystallization phenomenon. As previously mentioned, our glass is located in the Li_2O V_2O_5 V_2O_4 P_2O_5 quaternary system. It is noteworthy that V_2O_5 like P_2O_5 was considered as a possible glass former by Zachariasen [25]. Depending of

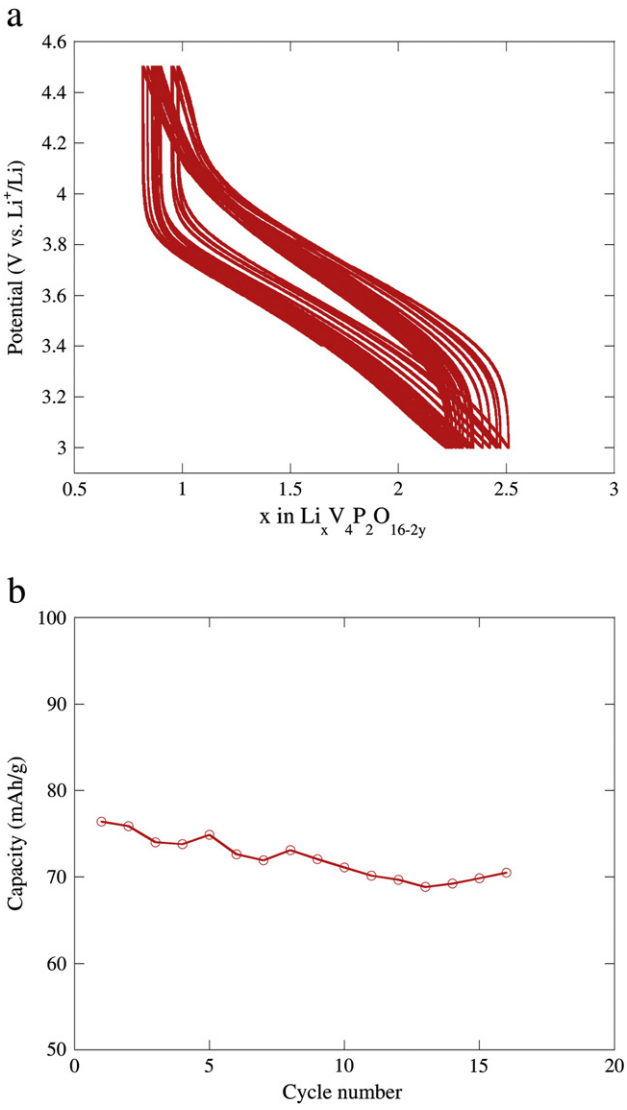

Fig. 6. (a) Galvanostatic charge/discharge curves of the $25Li_2O$-$50V_2O_5$-$25P_2O_5$ glass composition + 15%wt C for a voltage window [3–4.5 V], (b) Corresponding discharge capacity versus the cycle number of the cell.

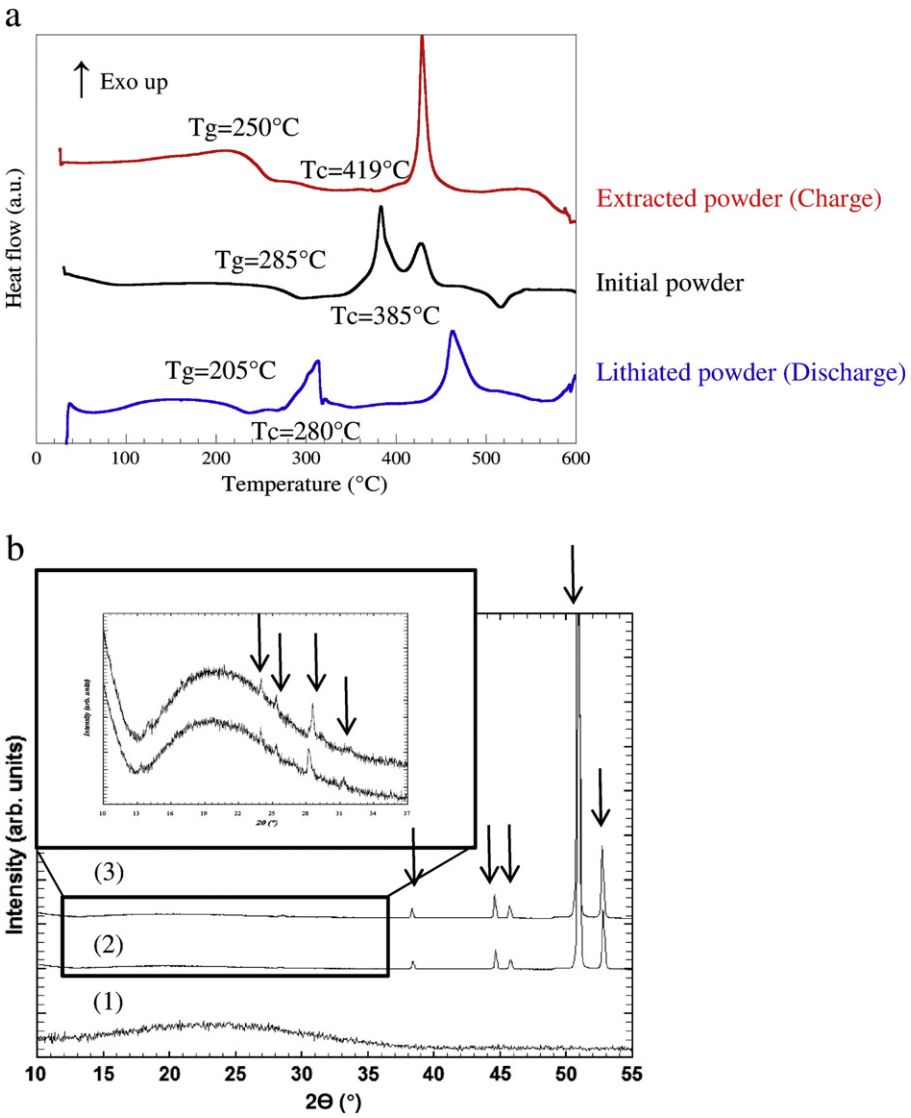

Fig. 7. (a) DSC measurements of the glass composition $25Li_2O$-$50V_2O_5$-$25P_2O_5$ and the chemically extracted (charged) and lithiated (discharged) glass. Glass transition temperature Tg and crystallization temperature Tc of the initial base glass $25Li_2O$-$50V_2O_5$-$25P_2O_5$ and the chemically extracted and inserted glass (DSC measurements) are mentioned by an arrow. (b) (1) Initial $25Li_2O$-$50V_2O_5$-$25P_2O_5$ glass powder, ex-situ XRD measurements of the initial $25Li_2O$-$50V_2O_5$-$25P_2O_5$ glass powder (2) and the same powder charged at 5 V (3). Diffraction peaks mentioned by an arrow correspond to the Al coated Be window.

the discharge depth, the insertion of Li into the glass tends to modify its composition toward the Li_2O V_2O_4/V_2O_3 P_2O_5 system. The increase of Li amount in the glass, as well as the increase of V_2O_4 (or V_2O_3), are known to destabilize the glass network. On the contrary, upon charge, we move to the ternary Li_2O V_2O_5 P_2O_5 system, with a decrease of Li content and the increase of V_2O_5, which will stabilize the glasses.

3.4. Discussion

As shown experimentally, the glass $25Li_2O$ $50V_2O_5$ $25P_2O_5$ exhibits interesting electrochemical properties when used at low potential, but also at high potential. While the use of non lithiated glassy electrodes as electrode material has already been investigated in the literature, the report of lithiated glassy material with electrochemical activities upon charge has, to our knowledge, not been widely considered. Moreover, it is difficult to find in the literature any crystalline oxophosphate compounds with a mixed valence (V^{4+}/V^{5+}) in the Li V P O systems. Amongst the existing materials, $LiVOPO_4$ [26,27], $Li_4VO(PO_4)_2$ [28] or $Li_2VOP_2O_7$ [29] can be considered for comparison. These crystalline materials require a multi step synthesis (precipitation + carbothermal reduction, preliminary chemical lithiation or ion exchange of hydrated or Na precursors). The obtained materials display electrochemical capacity from 30 $mAh.g^{-1}$ for $Li_2VOP_2O_7$, which presents an irreversible capacity associated to a structural modification to 70 $mAh.g^{-1}$ for $Li_4VO(PO_4)_2$ in presence of 50%wt of carbon, which is necessary to compensate the poor electronic conductivity of this material. Only β $LiVOPO_4$ displays a capacity of 135 $mAh.g^{-1}$ with some kinetic limitations and it requires cycling at low rates. It was shown how a small amount of V^{4+} in the α $VOPO_4$ increases its electronic conductivity and its electrochemical behavior [30]. The mixed valence of our glass plays an important role to guarantee the promising electrochemical performances. Such kind of glassy electrode materials offer many advantages, they are easy and fast to prepare with a large domain of existence, which allows modifying simply the chemical composition in comparison to crystalline phases. Moreover, the material remains glassy upon charge or discharge, with stabilization (large Tc Tg value) of the glass upon oxidation. The difference in glass transition temperatures between the initial base glass (Tg = 250 °C) and the corresponding extracted glass (Tg = 285 °C) is limited to only 35 °C (Fig. 7a) showing limited changes in the glass structure [31]. This could explain the good cycling of this glass composition when tested at high potential. Indeed,

there exists a strong correlation between the glass structure and the corresponding electrochemical performances [23].

4. Conclusion

The glass composition $25Li_2O\ 50V_2O_5\ 25P_2O_5$ has been tested as electrode material. This glassy material exhibits stabilized cycling be havior over 15 cycles with a capacity of 75 $mAh.g^{-1}$ when tested in the [3 4.5 V] potential windows. It is noteworthy that the glass remains amorphous upon cycling from 1.5 to 4.5 V. The ease and processing of glassy materials as well as the ability to modify slightly the composition without disturbing drastically the structure are great advantages over crystalline materials. Based on this preliminary study, the structure of this glass composition and other glasses in the $Li_2O\ V_2O_5\ V_2O_4\ P_2O_5$ system are now under investigation to se lect the optimized composition ensuring interesting electronic/ionic conductivities and a large content of lithium and vanadium to in crease the capacity upon charge. Glass ceramics with the presence of nano crystals inside the glassy matrix are also under investigations to enhance the electronic properties.

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